



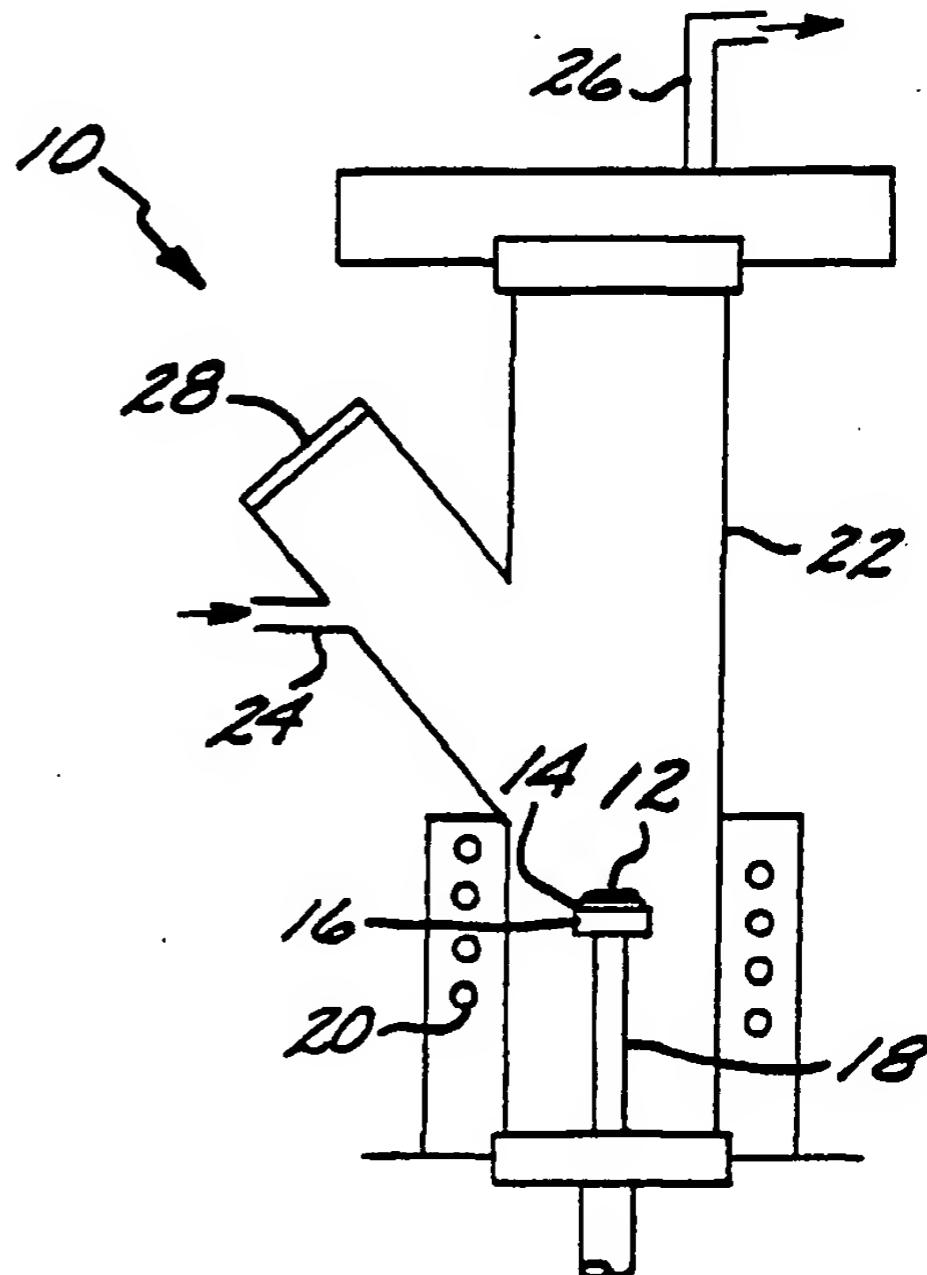
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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## (54) Title: PROCESS FOR DEPOSITING LAYERS OF DIAMOND

## (57) Abstract

A process for depositing diamond (12) onto a substrate (14), which is of particular utility in fabricating very thin layers of diamond. Diamond (12) is deposited by chemical vapor deposition of a hydrocarbon vapor wherein the carbon atoms are saturated and the ratio of hydrogen atoms linked to carbon atoms is less than 2. That is, the carbon atoms of the hydrocarbon are bonded by single bonds at an angle near 109.5 degrees, the same angle required for the carbon atoms in the deposited diamond. The limited number of hydrogen atoms ensures a compact structure for the hydrocarbon, and reduces the system burden of removing excess hydrogen upon deposition. The polycyclic alkanes exhibit the required structures. Preferred hydrocarbons include adamantane (Fig. 2), congressane (Fig. 3), cubane (Fig. 4), and basketane (Fig. 5).



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## PROCESS FOR DEPOSITING LAYERS OF DIAMOND

### BACKGROUND OF THE INVENTION

This invention relates to the deposition of thin films, and, more particularly, 5 to the deposition of thin films of diamond.

Diamond is an allotropic crystalline form of carbon wherein the carbon atoms are covalently bonded and arranged in a diamond cubic atomic lattice. Naturally occurring diamond is 10 found as polyhedral crystals and is familiar to most persons as a gemstone. Bulk diamond can also be manufactured synthetically, and both natural and synthetic diamonds are used in cutting tools and the like because diamond is hard and wear 15 resistant.

Diamond exhibits physical and chemical properties which make it potentially useful in microelectronic and optical devices. In such applications, typically the diamond would be 20 present as a thin layer, less than .001 inches thick, supported by a relatively thick substrate. The diamond layer might function as an active component of the device through which an electrical current or light passes, or might be a 25 passive element such as a heat sink, depending upon which of diamond's properties are to be used.

If diamond is to find widespread use in microelectronic and optical devices, techniques must be developed to deposit thin layers of 30 diamond onto substrates. Natural and synthetic bulk diamond cannot be used in these applications because layers less than a thousandth of an inch in thickness cannot be conveniently prepared from the bulk form and bonded to substrates.

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Thin layers of diamond can be deposited directly onto substrates by various techniques. For example, diamond layers can be deposited onto substrates by chemical vapor deposition, wherein a porous source material mixed with a carrier gas is passed over a heated substrate. With the correct source material and deposition conditions, a layer of diamond is deposited from the carbon atoms of the source material. The most widely used source material is methane, but carbon tetrachloride, acetone, alcohols, ethers, acetates, aldehydes, amines and other organic compounds have also been used with varying degrees of success.

Graphite, another allotropic form of carbon, is also deposited in thin layers by chemical vapor deposition. The reaction to deposit graphite competes with that to deposit diamond, and under many conditions graphite rather than diamond is deposited. Once deposited, the diamond is energetically favored to convert to graphite, but the reverse reaction of conversion of graphite to diamond is not thermodynamically favored. Thus, the deposition of a diamond layer can be interrupted by formation of graphite, which has completely different electrical, optical and physical properties and destroys the operability of the diamond layer for many applications. Both continuous and intermittent techniques have been developed for removing the graphite formed during the deposition of diamond, by introducing gaseous hydrogen into the chemical vapor deposition apparatus and reacting the hydrogen with the graphite to form methane.

The known techniques for depositing layers of diamond have relatively slow deposition rates, typically on the order of about one

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micrometer per hour. Such slow deposition rates inhibit the commercial exploitation of thin-film diamond technology. It is also necessary in most cases to interrupt the growth of the diamond layer 5 with intermittent hydrogen reaction cycles to remove any deposited graphite, or to dilute the source material gas with hydrogen for the same purpose. Existing processes for depositing thin layers of diamond are therefore slow and somewhat 10 unreliable, in part because other allotropic forms of carbon can be formed in the deposition process.

Accordingly, there exists a need for an improved approach for depositing thin layers or films of diamond onto substrates. The present 15 invention fulfills this need, and further provides related advantages.

#### SUMMARY OF THE INVENTION

The present invention is embodied in a process for depositing a layer of diamond onto a 20 substrate, which has a deposition rate greater than that of prior processes. The formation of graphite is greatly reduced, increasing the certainty that the deposited layer is purely diamond without any minute patches of graphite. 25 The perfection of the diamond layer and its epitaxy with the underlying substrate, important considerations for diamond layers used in microelectronic applications, are also improved.

In accordance with the invention, a 30 process for depositing a layer of diamond onto a substrate comprises furnishing a vapor of a hydrocarbon source material, the source material having all carbon atoms saturated and having a ratio of hydrogen atoms linked to carbon atoms of

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less than 2, and depositing the vapor of the source material onto the substrate, the substrate being heated to promote decomposition of the source material to form diamond on the surface of 5 the substrate.

The carbon atoms in a diamond cubic crystal structure are bonded to each other in a tetrahedral configuration by covalent single bonds wherein a single pair of electrons is shared by 10 the adjacent bonded carbon atoms. The angle between each of the bonds is about 109.5 degrees (or, more precisely,  $109^{\circ}28'$ ), which is determined geometrically as the angle between the adjacent rays extending from the center of a 15 regular tetrahedron to each of its vertices. The result of this geometry is an essentially three dimensionally bonded array of carbon atoms.

By contrast, the carbon atoms in graphite are arranged in parallel tiers about 3.4 20 Angstroms apart. The bonds between the carbon atoms in each tier are relatively strong, but the bond between the carbon atoms in adjacent tiers is relatively weak. The crystals in each tier are hexagonal plates that can be easily separated from 25 the crystals in adjacent tiers. Graphite therefore exhibits essentially a two-dimensional structure of weakly bonded plates that are arranged in a three-dimensional stack.

The structure of the vaporous source 30 material of the present invention is chosen to promote the formation of the deposited diamond structure rather than the graphite structure. The carbon atoms in the source material are bonded to each other by tetrahedrally arranged single bonds, 35 so that the natural tendency for each carbon atom is to form four tetrahedrally arranged single bonds to adjacent carbon atoms in the deposited

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layer. Simply stated, the source material is chosen to have a bond structure comparable with that of the deposited diamond, minimizing the need for the breaking, relaxation, and rearrangement of 5 carbon bonds upon deposition and the consequent energetic process.

By contrast, carbon atoms which have double or triple bonds in the vaporous state (or shared single/double bonds, as in aromatic 10 hydrocarbons) are converted to the deposited diamond form only by breaking the double or triple bonds and reforming the bonding structure of the carbon atoms to the tetrahedrally bonded state. This process requires the expenditure of 15 substantial energy for each carbon atom deposited, slowing the deposition process because an energy barrier must be surmounted with each deposited carbon atom. Moreover, the attempted deposition of source materials having double and triple bonds 20 requires that the deposition be essentially atom by atom, since each double or triple bond must be broken and rearranged as the atom is deposited. If the double or triple bond is not broken and rearranged during deposition, a not unexpected 25 occurrence in view of the energy required to break and rearrange the bond, a graphite structure likely results.

The ratio of the number of hydrogen atoms bonded to carbon atoms in the source 30 material of the invention is less than 2. The selection of this numerical maximum value for the ratio is not arbitrary, but is closely related to the possible hydrocarbon structures that may be used as the source material in conjunction with 35 the invention. The single-bond limitation, together with this limitation, exclude source materials that tend to form deposited graphite.

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For example, this limitation excludes the branched or unbranched straight-chain alkane hydrocarbons ( $C_nH_{2n+2}$ ), which have a ratio of linked hydrogen atoms to carbon atoms decreasing from 4 to 2 as  $n$  increases from 0, and the cyclic alkanes ( $(CH_2)_n$ ), which have a ratio of linked hydrogen atoms to carbon atoms of exactly 2. These and similar structures can pyrolyze in the gas phase to produce unsaturated derivatives, which in turn favor formation of aromatic hydrocarbons. The aromatic hydrocarbons tend to deposit in the two-dimensional graphite state, contrary to the desired result for the reasons stated previously.

The specification of a low ratio of linked hydrogen to carbon atoms also reduces the number of hydrogen atoms that must be removed from the vaporous source material upon deposition, relative to the total number of carbon atoms that are deposited. Reduction of the number of hydrogen atoms that must be removed in turn reduces the counterflow of hydrogen atoms from the surface of the substrate that tends to lower the deposition rate. Energetic requirements for breaking carbon-hydrogen bonds are also reduced.

The source materials are hydrocarbons, formed of hydrogen and carbon atoms. Related compounds containing other atoms substituted for the carbon or in functional groups are not used, except for considerations of doping to be discussed in the following paragraph. For example, oxygen-containing compounds (e.g., ethers, hydroxyls, carbonyls) are not used, as the included oxygen reacts with hydrogen to form water, which poisons the deposition. Similarly, nitrogen-containing compounds (e.g., amines) are not used.

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The hydrocarbon source materials can be codeposited with modified doped source materials containing small amounts of intended dopant atoms bonded to an otherwise hydrocarbon structure. Dopant atoms such as boron, phosphorus, or nitrogen can be incorporated into hydrocarbon molecules in a small, controlled amount to form doped source materials. These doped source materials are mixed with a larger amount of the pure hydrocarbon source material and codeposited, so that the diamond layer is continuously and uniformly doped with a small and controllable amount of the dopant as deposition proceeds. A subsequent, separate diffusional doping step is therefore not required.

In this doping approach, the dopant atoms are bonded into the structure that is selected to be favorable to deposition of diamond, according to the criteria set forth above. To be contrasted is the more common doping approach of mixing a separate gas with the hydrocarbon, as in the process of mixing a source material with a structurally different gas such as PH<sub>3</sub> for doping with phosphorus. The present invention is operable with either of these gaseous dopant approaches and with conventional diffusional doping, but the preferred technique is to use a dopant bonded into a hydrocarbon that structurally favors deposition of diamond.

The limitations of saturated tetrahedral carbon bonds and a ratio of linked hydrogen to carbon atoms of less than 2 are satisfied by the polycyclic alkanes. The preferred source materials of the invention, satisfying the stated limitations, are adamantane, congressane, cubane, and basketane. Each of these source materials has a sufficiently high vapor

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pressure in its solid or liquid form that operable amounts of vapor can be provided in a gas stream delivered to a reactor. Each molecule of these hydrocarbons has a plurality of carbon atoms, 5 joined to the other carbon atoms in a three-dimensional array approximating or matching that of deposited diamond. Adamantane and congressane are particularly preferred, as their core structure comprises carbon atoms with the 10 same diamond cubic arrangement and bond angle of 109.5 degrees as required for the deposited diamond film. The bonds of cubane and basketane are oriented at 90 degrees, and must be relaxed slightly for deposition as diamond.

15 Thus, a layer of diamond can be formed by stripping the hydrogen atoms from the adamantane or congressane molecule and depositing the remaining carbon atoms onto the surface without breaking or rearranging any of the 20 carbon-carbon bonds. The use of the preferred hydrocarbons increases the rate of deposition significantly as compared with the use of methane. Only one carbon atom is deposited per molecule of methane, while 10 carbon atoms are 25 deposited per molecule of adamantane, for example. Also, only 1.6 hydrogen atoms must be removed per carbon atom deposited for adamantane, and this ratio is 1.43 for congressane, 1.2 for basketane, and 1 for cubane. By contrast, for 30 methane, the source material most frequently used in the art, 4 hydrogen atoms must be removed per carbon atom deposited.

It will now be appreciated that the process of the present invention permits the 35 deposition of diamond layers more readily than by prior approaches. The carbon atoms of the hydrocarbon source materials are oriented to each

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other so as to readily deposit in the required diamond cubic structure, with a good geometric fit and without the need for breaking and reforming bonds. The reduced hydrogen content increases the 5 rate of deposition, as does the comparatively large size of the molecules. Other features and advantages of the invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with 10 the accompanying drawings, which illustrate, by way of example, the principles of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic side sectional view of a chemical vapor deposition apparatus for 15 practicing the invention;

Figure 2 is a perspective schematic view of the diamond crystal structure, with the carbon atoms of a molecule of adamantane superimposed and highlighted for reference;

20 Figure 3 is a perspective schematic view of the diamond crystal structure, with the carbon atoms of a molecule of congressane superimposed and highlighted for reference;

Figure 4 is a perspective schematic 25 view of the carbon atoms in a molecule of cubane; and

Figure 5 is a perspective schematic view of the carbon atoms in a molecule of basketane.

#### 30 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The properties of diamond make it

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highly desirable for use in certain semiconductor devices. Diamond can be employed as a heat sink because of its high thermal conductivity, which is about 5 times that of copper. A layer of diamond 5 below a heat-producing device, or a mass of diamond between devices, conducts heat rapidly away from the source. Heat-producing devices can therefore be packed more tightly on a chip.

The electrical properties of diamond 10 suggest its use as an active element of devices, particularly in devices to be used at elevated temperatures or in severe radiation environments. The band gap of diamond is 5.2 eV. Its hole mobility is about  $1600 \text{ cm}^2\text{sec}^{-1}\text{volt}^{-1}$ , while 15 the electron mobility is about  $2000 \text{ cm}^2\text{sec}^{-1}\text{volt}^{-1}$ . The charge carrier velocity is high, about  $2.3 \times 10^7 \text{ cm per second}$  at 20 kv per cm. Diamond is nonpolar, resulting in reduced charge carrier scattering. Diamond exhibits a 20 resistivity of about  $10^{13} \text{ ohm-cm}$ . Its breakdown voltage is  $10^7$  volts per centimeter. The dielectric constant is about one-half that of silicon.

Diamond also has optical and physical 25 properties of great interest. It is transparent over a broad range of wavelengths from the infrared through the near ultraviolet, and has an index of refraction of 2.38. Diamond is the hardest natural material, making it resistant to 30 physical damage. It is radiation hard and has a low scattering cross section. Its melting point is over  $3500^\circ\text{C}$ , and it does not transform at lower temperatures. Diamond therefore has great potential for use in semiconductor and 35 electro-optical devices, particularly those required to resist high temperatures and radiation exposure. Thin films of diamond can also be

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expected to find use as a wear-resistant layer over softer materials, as in machine tools, drills, gems, etc.

To realize many of the most promising 5 applications of diamond, a technique for rapidly depositing thin, high quality layers of diamond is necessary. In its preferred embodiment, the present invention uses chemical vapor deposition to deposit a thin layer of diamond. Generally, in 10 chemical vapor deposition a substrate, upon which the layer is to be deposited, is heated or otherwise activated so that a reactant source gas passed over the surface decomposes and deposits atoms to the growing film.

15           Figure 1 illustrates an apparatus 10 suitable for the chemical vapor deposition of a diamond layer 12 upon a substrate 14. The substrate is mounted in a conducting holder 16, which can be heated by conduction along a pedestal 20 18. The pedestal may be mounted to permit its rotation, thereby encouraging uniform deposition of the layer 12. Alternatively, and as shown in Figure 1, the holder 16 also acts as a susceptor and is heated by the radio frequency signal 25 applied to an rf coil 20 that surrounds the holder 16. The rf signal also influences the source gas from which deposition occurs, probably by activating the gas phase molecules to promote their decomposition. Specifically, the hydrogen 30 atoms are stripped from the hydrocarbon gas molecules by the elevated temperature and radio frequency power of the rf coil 20.

The substrate 14, holder 16 and support 18 are placed inside a reactor tube 22, 35 which is typically a nonconductive glassy material such as fused quartz or a ceramic such as silica that is resistant to chemical attack by the source

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gas. A gas flow is introduced into the interior of the reactor tube through an inlet 24, permitted to flow past the substrate 14, and removed through an outlet 26. A view port 28 is provided so that 5 the deposition can be monitored visually.

A source gas containing a hydrocarbon, from which the carbon atoms are deposited to the growing diamond layer 12, is introduced in a mixture with a carrier gas, normally hydrogen. 10 The mixture of source gas and carrier gas is prepared by passing hydrogen over a solid source of the source gas or bubbling hydrogen through a liquid source of the source gas, so that a controlled amount of the source gas vaporizes 15 under the driving force of the solid or liquid vapor pressure. The quantity of the source gas in the gas stream is controllable, using established techniques, by varying the flow rate of the carrier gas, and the temperature of evaporation. 20 Typically, the hydrocarbon-containing source gas comprises from about 1 to about 4 percent by volume of the total gas stream.

Two or more source gases can be mixed with the carrier gas to form the gas stream that 25 is flowed past the substrate 14. For example, a second hydrocarbon source gas may be mixed with the source gas of the invention to improve deposition rate or stoichiometry of the deposited diamond layer 12. The second hydrocarbon source 30 gas could be a second source gas in accordance with the invention, or could be a source gas that is not in accordance with the invention, such as methane. A second source gas that is not a pure hydrocarbon can also be mixed into the gas stream, 35 as a means of doping the diamond layer 12. This source gas could contain dopants such as nitrogen, phosphorus or boron bonded into the gas phase

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molecules, so that the dopant is continuously and evenly introduced into the layer 12 as it is deposited. With this approach, doping of the layer 12 after deposition could be avoided.

5                 Figure 2 depicts the diamond crystal structure that must be obtained in the layer 12. The structure of diamond can be viewed as a regular repeating three-dimensional arrangement of carbon atoms tetrahedrally bonded to neighboring  
10 carbon atoms by single bonds. In this bonding arrangement, the carbon orbitals are in the  $sp^3$  state. The angles between the four bonds of any one carbon atom are all about 109.5 degrees, as dictated by the tetrahedral geometry.

15                 One preferred source material for providing the source gas is adamantane, having the gross molecular composition of  $C_{10}H_{16}$ . The structure of the carbon atoms in adamantane is also illustrated in Figure 2, as the shaded atoms  
20 superimposed upon the diamond structure. The adamantane molecule is not linear in form, but instead is more compact with four of the carbon atoms bonded to three other carbon atoms. (The remaining six carbon atoms are each bonded to two  
25 other carbon atoms.) Another result of the bonding of some carbon atoms to more than two other carbon atoms is that the number of bonded hydrogen atoms per carbon atom is, on the average, less than two. Adamantane is formed of 10 carbon  
30 atoms each tetrahedrally bonded by single bonds, with the angles between the carbon bonds 109.5 degrees. Those electrons of the carbon atoms not participating in the bonds to other carbon atoms help bond hydrogen atoms to the carbon atoms,  
35 saturating the carbon atoms.

The carbon atoms of adamantane are thus tetrahedrally bonded with the carbon orbitals.

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in the  $sp^3$  state, just as required for forming the diamond structure. There is no breaking or rearrangement of the carbon-carbon bonds required in forming the diamond structure from adamantane molecules. A unit of the diamond structure can be formed by removing the hydrogen atoms from a molecule of adamantane and depositing the remaining carbon atoms directly onto a growing layer of diamond. Ten carbon atoms are added to 10 the diamond layer for each molecule so deposited. By comparison, only a single carbon atom is added for each molecule of methane deposited by conventional procedures for growing diamond layers.

15 Another preferred source material is congressane, whose structure is illustrated in Figure 3 superimposed upon the diamond structure. Congressane, with a gross molecular formula of C<sub>14</sub>H<sub>20</sub>, has tetrahedrally bonded carbon atoms like adamantane, and consequently has the same advantages of adamantane as discussed previously.

Some other, more complex hydrocarbon molecules are expected to have their carbon atoms all tetrahedrally bonded, in the  $sp^3$  state with 25 bond angles of 109.5 degrees. However, increasing the atom mass of a molecule ordinarily decreases its vapor pressure, so that it becomes increasingly difficult to introduce a sufficient amount of the vapor into the carrier gas stream to 30 attain high deposition rates of the layer 12. Adamantane is the molecule of the lowest mass presently known, which also has the carbon atoms tetrahedrally bonded with 109.5 degree bond angles and a ratio of hydrogen atoms linked to carbon 35 atoms of less than 2.

Other hydrocarbon molecules are known wherein the carbon atoms are saturated and have

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less than 2 hydrogen atoms per carbon atom. However, these molecules have bond angles of the carbon bonds distorted to angles other than 109.5 degrees, and the carbon-carbon bond angles must be 5 relaxed in order to form the diamond structure. In this respect such molecules are less favored than adamantane and congressane, but in other respects are more favored. Specifically, these other hydrocarbons have lower ratios of numbers of 10 hydrogen atoms to carbon atoms than do adamantane and congressane, and also have higher vapor pressures because of their lower atomic weights. Consequently, they are also preferred embodiments 15 of the invention. The selection of the exact hydrocarbon to be used depends upon the circumstances of the deposition.

One such hydrocarbon is cubane, whose structure is illustrated in Figure 4. Cubane, whose gross molecular formula is C<sub>8</sub>H<sub>8</sub>, has 20 carbon-carbon bond angles of 90 degrees. Each carbon atom is bonded by a single bond to three other carbon atoms, and has one hydrogen atom to saturate the remaining bond. It is apparent that the carbon-carbon bonds must be at least 25 rearranged to produce the diamond structure having 109.5 degree bond angles. However, only single bonds are involved, and the rearrangement is small. In principle, opening two parallel edges of the cubane molecule provides the freedom for 30 the carbon-carbon bond couples to relax from 90 degrees to 109.5 degrees. Cubane, like adamantane, has the three-dimensional bond structure that promotes formation of the three-dimensional diamond structure in preference 35 to the two-dimensional graphite structure. The ratio of hydrogen atoms to carbon atoms in cubane is one, even smaller than for adamantane.

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A variation of cubane is basketane, whose gross molecular structure is C<sub>10</sub>H<sub>12</sub>. The molecular structure of basketane is illustrated in Figure 5, and is seen to be a 5 variation of cubane wherein two carbon atoms have other carbon atoms substituted for the hydrogen atoms. In basketane, two carbon atoms are bonded to two other carbon atoms each, and eight carbon atoms are bonded to three other carbon atoms 10 each. The remaining carbon orbitals bond hydrogen atoms. As with cubane, the carbon atoms have bond angles which are not 109.5 degrees. The rearrangement of carbon-carbon bonds is required to deposit diamond from basketane, although, as 15 with cubane, only single bonds are involved, and the relaxation of the bond angles is small. Like cubane, the ratio of hydrogen atoms to carbon atoms is low, in the case of basketane 1.2. The orbital bond state for cubane and basketane is 20 thought to be a hybridization of the sp<sup>3</sup> state. Such an intermediate hybridization would be of a high free energy, so that it is relatively easy to "open" the molecule and relax the bond angles to the required 109.5 degree orientation and sp<sup>3</sup> 25 state.

A further reduction in the number of hydrogen atoms might yield benefits in increased vapor pressure of the source material, but small molecules tend to be geometrically limited in 30 undesirable ways so that the carbon-carbon bond angles are very different form that of diamond. The hydrocarbons of lower mass contribute fewer carbon atoms per molecule deposited. Even more significantly, the lower mass hydrocarbons may 35 strongly favor the deposition of a graphite structure in preference to a diamond structure. For example, hydrocarbons based upon the benzene

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structure have carbon atoms which are not tetrahedrally bonded and therefore do not meet the requirements of the present invention. Polyacenes, which are condensation products of 5 benzene, form a two dimensionally bonded structure resulting in a three-dimensional stack of plates characteristic of graphite. Deposition of graphite is therefore favored.

Careful selection of the hydrocarbon 10 source material for chemical vapor deposition yields important benefits in promoting a diamond structure in preference to a graphite structure. Gas molecules having tetrahedrally bonded carbon atoms in three-dimensional arrays, with bond 15 angles between the carbon atoms of about 109.5 degrees, the bond angle in diamond, favor the deposition of diamond in preference to graphite. Little or no rearrangement of the bonds is required for such vaporous sources. The amount of 20 hydrogen that must be removed from the vicinity of the deposition is also reduced, increasing the deposition rate. Four particular preferred hydrocarbons have been identified as meeting the requirements, adamantane, congressane, cubane and 25 basketane, although it is expected that other hydrocarbons will be found that also meet the requirements. Although a particular embodiment of the invention has been described in detail for purposes of illustration, various modifications 30 may be made without departing from the spirit and scope of the invention. Accordingly, the invention is not to be limited except as by the appended claims.

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CLAIMS

What is claimed is:

1. A process for depositing a layer of diamond onto a substrate, comprising the steps of:
  - furnishing a vapor of a hydrocarbon source material, the source material having all carbon atoms saturated and having a ratio of hydrogen atoms linked to carbon atoms of less than 2; and
  - depositing the vapor of the source material onto the substrate, the substrate being heated to promote decomposition of the source material to form diamond on the surface of the substrate.
2. The process of claim 1, wherein the source material is selected from the group consisting of adamantane, congressane, cubane, and basketane.
3. The process of claim 1, wherein the vapor of the source material is mixed with a vapor of a compound containing dopant atoms.
4. The process of claim 1, wherein the substrate is selected from the group consisting of diamond, silicon, silicon dioxide, molybdenum, gallium arsenide, and aluminum oxide.
5. The process of claim 1, wherein said step of depositing is accomplished with the substrate in a radio frequency field.
6. The process of claim 1, wherein said step of depositing includes the substeps of

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mixing the vapor of the starting material with a carrier gas, and  
5 flowing the mixture of the vapor and the carrier gas over the substrate.

7. A process for depositing a layer of diamond onto a substrate, comprising the steps of:

furnishing a vapor of a hydrocarbon source material wherein all carbon atoms are bonded by  $sp^3$  hybridized orbitals, and the ratio of hydrogen atoms linked to carbon atoms is less than 2; and

10 decomposing the vapor of the source material at the surface of the substrate to deposit the carbon atoms onto the substrate, and releasing the hydrogen atoms.

8. The process of claim 7, wherein the source material is selected from the group consisting of adamantane, congressane, cubane, and basketane.

9. The process of claim 7, wherein the vapor of the source material is mixed with a vapor of a compound containing dopant atoms.

10. The process of claim 7, wherein the substrate is selected from the group consisting of diamond, silicon, silicon dioxide, molybdenum, gallium arsenide, and aluminum oxide.

11. A process for depositing a layer of diamond onto a substrate, comprising the steps of:

furnishing a starting vapor of a 5 compound selected from the group consisting of adamantane, congressane, cubane and basketane; and

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reacting the starting vapor with the substrate by chemical vapor deposition to deposit diamond onto the substrate.

12. The process of claim 11, wherein the starting vapor is mixed with a vapor of a compound containing dopant atoms.

13. The process of claim 11, wherein the substrate is selected from the group consisting of diamond, silicon, silicon dioxide, molybdenum, gallium arsenide, and aluminum oxide.

14. The process of claim 11, wherein said step of reacting is accomplished with the substrate in a radio frequency field.

15. The process of claim 11, wherein said step of reacting includes the substeps of

mixing the starting vapor with a carrier gas, and

5 flowing the mixture of the starting vapor and the carrier gas over the substrate.

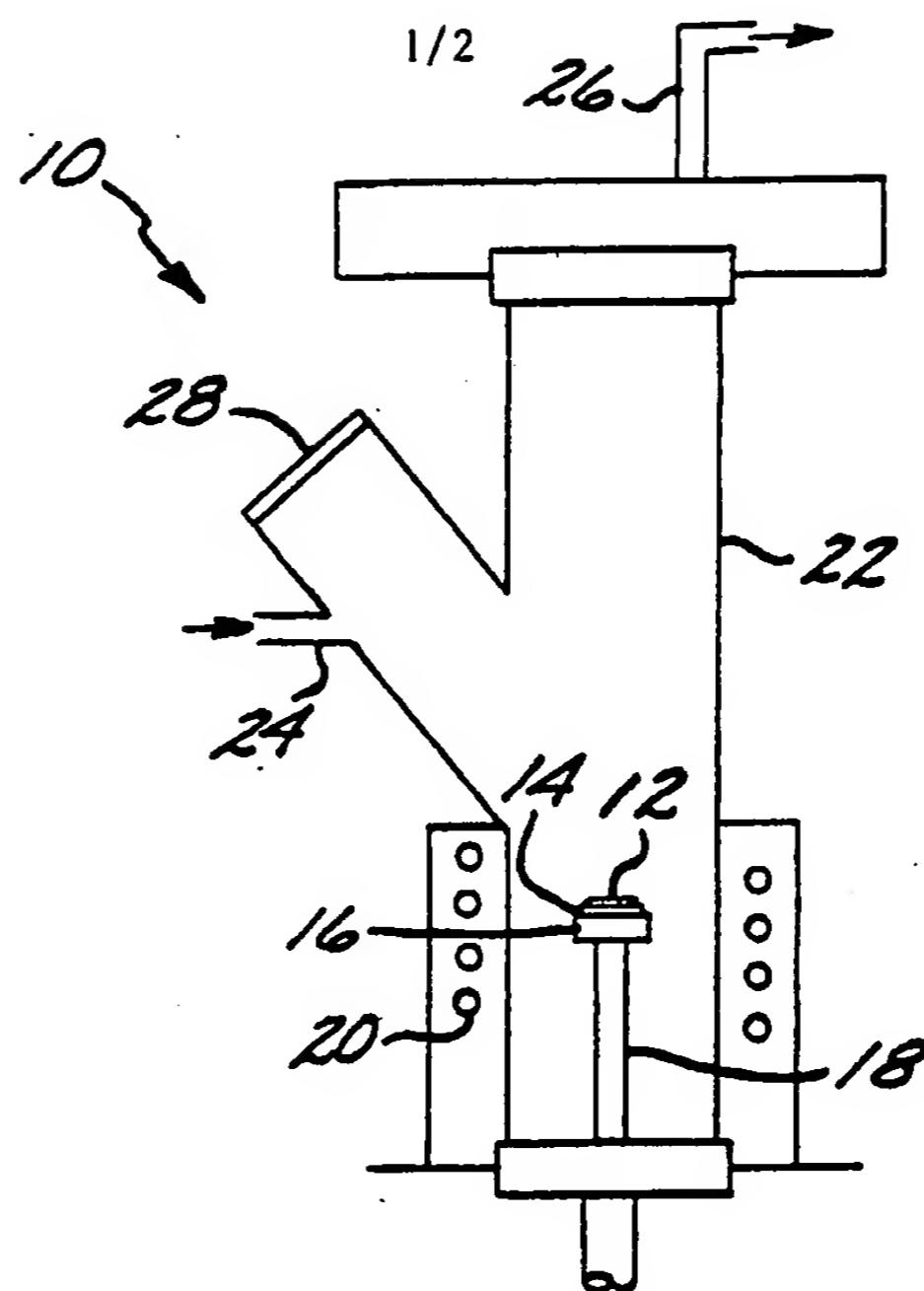


FIG. 1

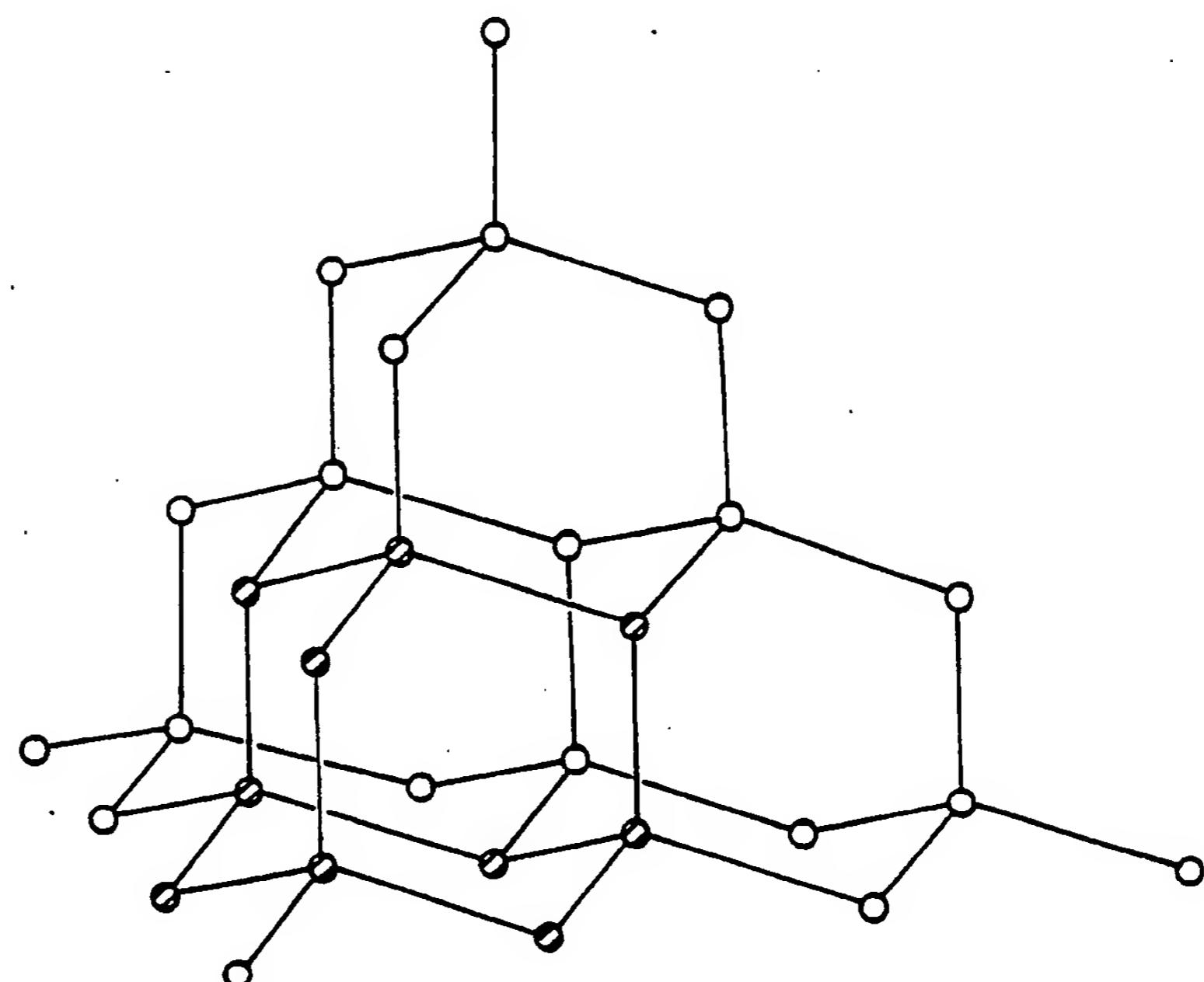


FIG. 2

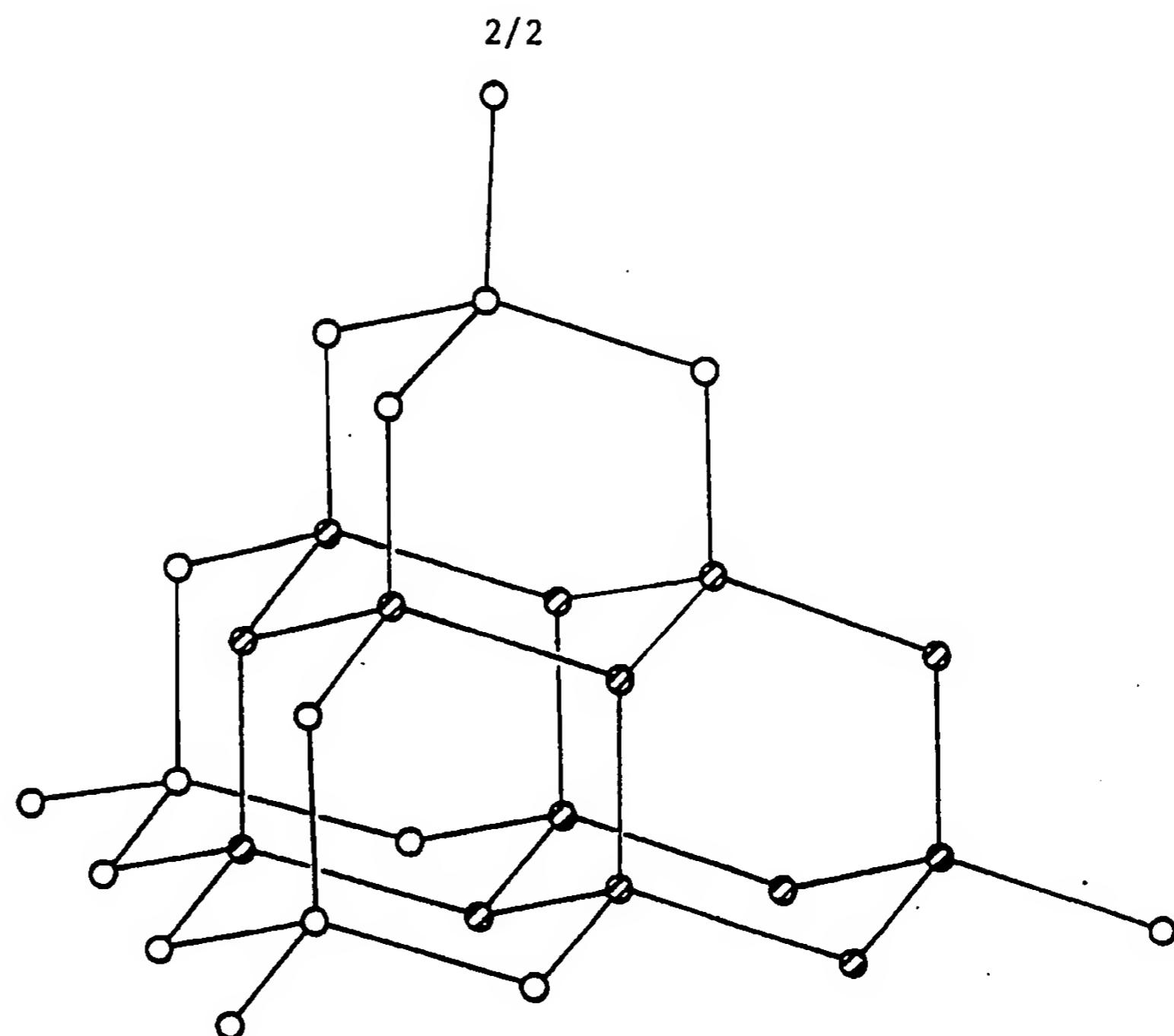


FIG.3

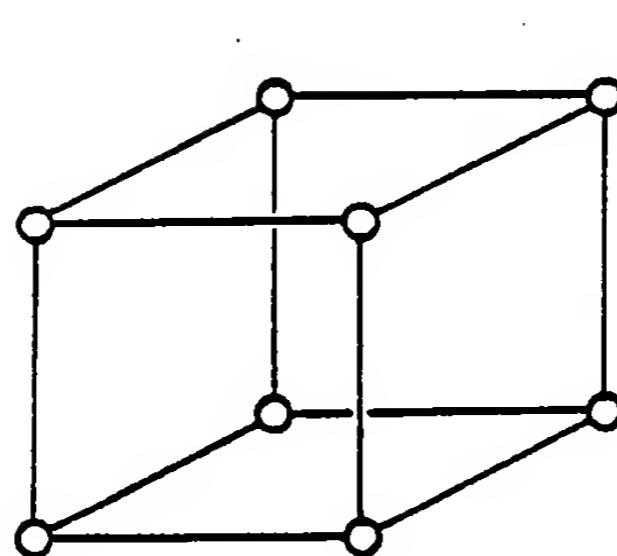


FIG.4

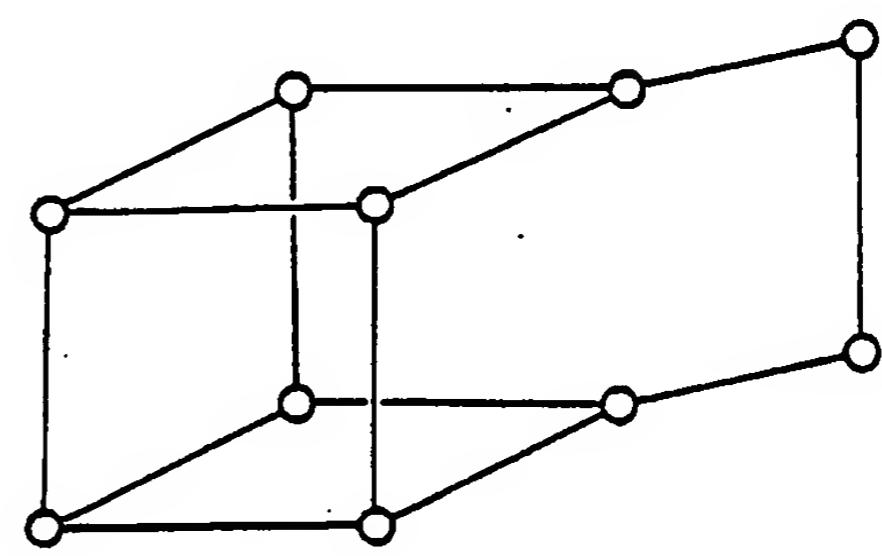


FIG.5

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/02251

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC<sup>4</sup>** : C 23 C 16/26; C 30 B 25/02; C 30 B 29/04

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
<b>IPC<sup>4</sup></b>	C 23 C; C 30 B

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. ***
Y	Chemical Abstracts, volume 105, no. 12, 22 September 1986, (Columbus, Ohio, US) D.V. Fedoseev: "Deposition of poly- meric films from diamond structure fragments under the influence of an electric discharge", see page 33, abstract 98417a, & Kolloidn. Zh. 1986, 48(3), 609-10	1,4,7,10
A	--	2,8,11,13
A	GB, A, 2099806 (THE SECRETARY OF STATE FOR DEFENCE) 15 December 1982 see abstract; figures 1,2	1,4,7,10
A	see page 1, lines 78-97	5,14
A	--	
A	US, A, 3362788 (J.L. LAUER) 9 January 1968 see claims 1-21	1-3,4,7- 13
A	--	
A	EP, A, 0161829 (IMAI YOSHIO) 21 November 1985 see claims 1,16	3,6,9,12, 15
	--	

\* Special categories of cited documents: \*\*

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

10th February 1988

Date of Mailing of this International Search Report

22 MAR 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

P.C.G. VAN DER PUTTEN

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstracts of Japan, volume 9, no. 267 (C-310)(1990), 24 October 1985, & JP, A, 60114571 (MITSUBISHI KINZOKU K.K.) 21 June 1985 --	3,6,9,12, 15
A	Chemical Abstracts, volume 103, no. 13, 30 September 1985, (Columbus, Ohio, US) see page 644, abstract 244988m, & JP, A, 60127293 (ASAHI CHEMICAL INDUSTRY CO., LTD) 6 July 1985 --	1,6
A	Journal of Applied Physics, volume 60, no. 4, 15 August 1986, American Institute of Physics, (Woodbury, New York, US), K. Noda et al.: "Characteristics and boron doping effect of hydrogenated amorphous carbon films", pages 1540- 1542 see page 1540, abstract -----	7

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8702251  
SA 19368

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 07/03/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2099806	15-12-82	None	
US-A- 3362788		None	
EP-A- 0161829	21-11-85	JP-A- 60221395	06-11-85